

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



International defeat

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT) WO 97/20020 (51) International Patent Classification 6: (11) International Publication Number: A1 C11D 3/12, 3/22 5 June 1997 (05.06.97) (43) International Publication Date: (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, (21) International Application Number: PCT/EP96/04886 BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU. IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS. 7 November 1996 (07.11.96) (22) International Filing Date: LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT. RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG). (30) Priority Data: Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). EP 29 November 1995 (29.11.95) 95203280.3 European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, (34) Countries for which the regional or GR. IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, international application was filed: NL et al. CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). (71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Published With international search report. Rotterdam (NL). (71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4 4BQ (GB). (72) Inventors: ARTS, Theodorus, Johannes, Comelis; Crosfield B.V., Ir. Rocourstraat 28, NL-6245 AD Eijsden (NL). AUGUSTIJN, Govert, Johannes; DiverseyLever, Maarssenbroeksedijk 2, NL-3606 AN Maarssen (NL). CONNOTTE, Hendrik, Johannes, J.; DiverseyLever, Maarssenbroeksedijk 2, NL-3606 AN Maarssen (NL). OSINGA, Theo, Jan; Crosfield B.V., Ir. Rocourstraat 28, NL-6245 AD Eijsden (NL).

(54) Title: DETERGENT BUILDER GRANULE

(57) Abstract

A builder granule suitable for use in a particulate detergent composition is provided, comprising: 50-90 % by weight of a zeolite; 0-25 % by weight of a nonionic surfactant; 1-10 % by weight of alkalimetal carboxycellulose having a purity of more tha 80 % by weight; and up to 20 % by weight of water. Said builder granule has favourable dispensability and dispersability characteristics when used in a detergent formulation.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
ΑT	Austria	GE	Georgia	MX	Mexico
ΑÜ	Australia	G.N	Guinea	NE	Niger
ВВ	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	1E	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
ВJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic	SD	Sudan
CF	Central African Republic		of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	ΚZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	1.R	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	1.0	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	1T	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML.	Mali	US	United States of America
FR	France	MN	Mongolia	UZ.	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Vict Nam

DETERGENT BUILDER GRANULE

Field of the invention

5 The present invention relates to detergent builder granules, more particularly zeolite builder granules. The invention also relates to detergent compositions including such granules.

10 Background of the invention

Zeolites of the molecular sieve type have commonly been employed in cleansers, particularly in laundry detergent compositions, as a builder to provide a water softening function, when the detergent or cleanser is placed in an aqueous solution. Zeolites have more recently been employed

15 aqueous solution. Zeolites have more recently been employed to replace phosphate builders.

Generally, zeolites have been found to be relatively difficult to employ in dry-mixed detergent compositions,

20 for a number of reasons. Difficulties arising during manufacture of detergent compositions with zeolite have often been related to the fine particle size of the crystalline zeolites.

Typically, zeolites have a particle size of approximately 1-20 microns. Thus, if the zeolite is used in its normal state with such a particle size, it commonly presents problems with dusting and segregation in the detergent composition.

30 For this reason it has been found to be generally desirable in prior practice to agglomerate the zeolite either by itself or with other detergent constituents prior to incorporation into the detergent composition. Such agglomerated zeolite granules as well as processes for

35 their manufacture are well-known in the art.

WO 97/20020

2

PCT/EP96/04886

For instance, EP-A-403,084 (Clorox) discloses a method of forming a zeolite agglomerate, including the steps of blending zeolite particles with a filler and a surfactant, and then agglomerating the thus formed blend in a rotary agglomerator with a zeolite binder. The zeolite agglomerate is subsequently combined with other detergent constituents in a second agglomeration step to form a granular detergent product with minimal segregation and dusting. Silicate and polyacrylate are mentioned as preferred binding agents.

10

EP-A-368,364 and EP-A-279,038 (Degussa) disclose other types of zeolite granules comprising crystalline zeolite material and relatively small amounts of nonionic surfactant and carboxymethyl cellulose.

15

Although these zeolite granules of the prior art have generally favourable properties, we have found that their dispersability and dispensability in the wash liquor when applied in a detergent formulation, often leaves to be

20 desired.

Consequently, it is an object of the present invention to provide a type of zeolite granules having good dispensability and dispersability characteristics when used in a detergent formulation.

- 25 It is another object to provide a type of zeolite granule which has a good influence on the dispensing behaviour of the particulate detergent composition in which it is present.
- 30 We have now surprisingly found that these and other objects are achieved by the type of builder granule according to the present invention, including, as a binding agent, carboxymetyl cellulose of increased purity.

Definition of the present invention

Accordingly, in a first aspect the present invention provides a builder granule suitable for use in a particulate detergent composition, comprising:

5 50 - 90% by weight of zeolite material;

0 - 25% by weight of a nonionic surfactant;

1 - 10% by weight of alkalimetal carboxymethyl cellulose, having a purity of more than 80% by weight,

up to 20% by weight, preferably 5-12% by weight, of water.

10

In a second aspect, the present invention provides a particulate detergent composition, comprising one or more nonionic and/or anionic surfactants and builder granules according to the present invention.

15 To avoid dustyness and segregation phenomena in said particulate detergent composition, the builder granule of the present invention has an average particle size which is generally in the range of 180-2000 microns, an average particle size of 200-800 microns being preferred.

20

Detailed description of the invention

The binding agent

Alkalimetal carboxymethyl cellulose (CMC), preferably

25 sodium carboxymethyl cellulose, is used as a binding agent
in the builder granule of the present invention. It was
found that the purity of carboxymethyl cellulose determines
to a large extent the disintegration and dispersion
properties of the builder granule of the invention. The CMC

30 in the builder granule should have a purity of at least 80%
by weight, preferably at least 85% by weight. A purity of
at least 90% by weight is more preferred, the remainder of
the CMC being mainly salts and absorbed water.

The level at which the CMC is present in the builder

The level at which the CMC is present in the builder 35 granule of the invention, is generally 1-10% by weight, whereas a level of 3-5% by weight is preferred.

The nonionic surfactant in the granule

The builder granule of the invention further contains a level of up to 25% by weight of a nonionic surfactant. If the builder granule is applied as such, for instance as 5 water softener, then it preferably does not contain any nonionic surfactant.

If the builder granule of the invention is applied as a constituent of a particulate detergent formulation, then it contains nonionic surfactant material at a level of

- 10 preferably 5-25%, more preferably 10-20% by weight. It was found that not only the purity of the CMC but also the type of nonionic surfactant used in the granule according to the present invention affect the desired disintegration and dispersion properties of the granule
- 15 significantly. More particularly, it was found that these properties were improved when a low meso-phase forming type of nonionic surfactant was applied. The best results were obtained in this respect when a non meso-phase forming nonionic surfactant was used as a major constituent of the 20 granules of the invention.
 - A low meso-phase forming surfactant is defined as a type of surfactant which does not show substantial gel-formation when diluted with water, whereas a non meso-phase forming surfactant does not show substantial viscosity increase
- 25 when diluted with water.

Suitable types of nonionic surfactants for use in the builder granule of the invention, are fatty alcohol ethoxylates having an average of 3 - 8 ethylene oxide groups per molecule. Preferred fatty alcohol ethoxylates 30 are non or low meso-phase forming.

The zeolite material

The zeolite material which is present in the builder granule of the invention at a level of 50-90%, preferably 35 60-90%, more preferably 70-80% by weight, can be a crystalline sodium aluminosilicate detergency builder, as described, for example, in GB 1 429 143 (Procter & Gamble). Suitable sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

5

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite material incorporated in the builder granule of the invention is maximum aluminium zeolite P (zeolite MAP), as described and claimed in EP-A-384,070 (Unilever). Zeolite MAP is defined as an alkalimetal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is

20 generally at least 150 mg CaO per gram of anhydrous material, as measured according to method 1 as disclosed in EP-A-384,070.

For several reasons, zeolite MAP is most preferred for use in the builder granules of the present invention.

Because of the superior dispersion properties of zeolite MAP, an even lower residue was observed to be obtainable with builder granules including zeolite MAP than with zeolite 4A granules. As a consequence, the risk that detergent residue remains on the fabric after the wash, is considerably reduced when applying builder granules of the invention including zeolite MAP as a constituent of a

invention including zeolite MAP as a constituent of a detergent formulation.

Furthermore, zeolite MAP has a lower water content than

35 commercially available zeolite 4A; zeolite MAP has a water level below 18%, whereas zeolite 4A has a water level above

18%. Moreover, the water vapour pressure of zeolite MAP is clearly lower than of zeolite 4A.

Because of this lower water content and lower water vapour pressure, the storage stability of bleaches, bleach

5 precursors and enzymes present in detergent formulations also containing zeolite MAP granules of the invention, can be improved.

Zeolite MAP granules have lower friability values than zeolite 4A granules, indicating that zeolite MAP is a

10 stronger type of zeolite. Therefore, detergent formulations including builder granules of the invention containing zeolite MAP have improved properties such as dynamic flow rate and compressibility. Furthermore, the particle size distribution of said formulations may be more uniform and

15 therefore less sensitive to powder segregation, than with builder granules containing zeolite 4A.

Because of the different structure and smaller particle size of zeolite MAP, the liquid carrying capacity of 20 builder granules including zeolite MAP is relatively high, as compared to builder granules including zeolite 4A. Therefore, detergent formulations with high liquid surfactant percentages can be made via simple dry-mixing, when applying zeolite MAP in the builder granules of the 25 invention.

Production process and use

The builder granules of the invention are effectively produced by granulating zeolite material with the other 30 constituents of the granules in a low speed mixer/granulator such as a V-blender, a PK Niro Zigzag granulator or a rotating drum. Alternatively, this granulation process is carried out in a high speed mixer/granulator such as a FUKAE mixer, a VOMM turbo 35 granulator, a Schugi Flexomix or a Lödige ploughshare mixer. Subsequently, the thus formed granules are dried in

....

a fluid bed and sieved to obtain the required particle size distribution.

The bulk density of the builder granules of the invention is typically in the range of 300-800 g/l, more preferably in the range of 400-700 g/l. The bulk density of the produced builder granules could be effectively controlled by incorporating therein a spray-dried amorphous alkalimetal silicate (desirably having a density of 50-600 g/l) at a level of 0.5-25%, more preferably 0.5-10% by weight. Preferred spraydried amorphous alkalimetal silicates are sodium silicates having a SiO₂ to Na₂O mol ratio being in the range of 1.7 - 3.4, sodium silicates having a SiO₂ to Na₂O mol ratio in the range of 1.7 to 2.4 being most preferred.

The builder granules may be used for producing a wide range of particulate detergent formulations, via the dry-mixing route. The detergent formulation of the invention desirably comprises a peroxy bleach and one or more anionic and/or nonionic surfactants, in addition to the builder granules of the invention. These builder granules are preferably present in said formulation at a level of 20-80% by weight.

25 Surfactants

The total amount of anionic and/or nonionic surfactant present in the detergent composition of the invention will preferably range from 5 to 40% by weight, more preferably from 10 to 30% by weight and especially from 10 to 20% by weight. These figures are typical for fully formulated detergent compositions.

The detergent composition of the invention preferably contains one or more nonionic surfactants. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the $\rm C_{12}$ - $\rm C_{15}$

WO 97/20020 PCT/EP96/04886

8

primary and secondary alcohols ethoxylated with an average of from 3 to 20 moles of ethylene oxide per mole of alcohol. Primary and secondary alcohol alkoxylates also containing propylene oxide groups and/or butylene oxide groups as well as end-capped alkoxylates may also be used as a constituent of the detergent composition of the invention.

In addition, anionic surfactants may be present at a level of up to 20% by weight, said level being desirably in the range of from 1 to 10% by weight, these figures being based on a fully formulated detergent composition.

Anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates,

15 particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅; primary and secondary alkyl sulphates, particularly sodium C₁₂-C₁₅ primary alcohol sulphates; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

Bleaching agent

The detergent composition of the invention may also comprise a bleach component, encapsulated or not, in an 25 amount of up to 30% by weight. Said bleach component may be a hypohalite bleach such as NaDCCA, or a peroxygen compound, i.e. a compound capable of yielding hydrogen peroxide in aqueous solution.

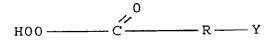
For environmental reasons, a peroxygen compound selected from alkali metal peroxides, organic peroxides, such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates, is preferably used. Mixtures of two or more of such compounds may also be suitable.

Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons.

The peroxygen bleach compound is suitably present in the detergent composition of the invention at a level of up to 25% by weight, preferably of from 5 to 20% by weight.

On the other hand, if present the hypohalite bleach may be suitably used in an amount of up to 10%, preferably 1-5% by weight, as active chlorine.

Organic peroxyacids may also be suitable as peroxygen bleaching agent. Such materials normally have the general formula:



wherein R is an alkylene or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or

25 C 00H

group or a quaternary ammonium group.

- 30 Typical monoperoxy acids useful herein include, for example:
 - (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy- α -naphthoic acid;

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxylauric acid, peroxystearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and (iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

5

Typical diperoxyacids useful herein include, for example:

- (iv) 1,12-diperoxydodecanedioic acid (DPDA);
- (v) 1,9-diperoxyazelaic acid;
- 10 (vi) diperoxybrassilic acid; diperoxysebasic acid and
 diperoxyisophthalic acid;
 - (vii) 2-decyldiperoxybutane-1,4-diotic acid; and
 (viii) 4,4'-sulphonylbisperoxybenzoic acid.
- 15 Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS).

 If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10 % by weight, preferably from 20 4-8 % by weight.
 - All these peroxide compounds may be utilized alone or in conjunction with a peroxyacid bleach precursor.
- 25 Peroxyacid bleach precursors are known and amply described
 in literature, such as in the British Patents 836988;
 864,798; 907,356; 1,003,310 and 1,519,351; German Patent
 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and US
 Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and
 30 4,675,393.

Another useful class of peroxyacid bleach precursors is that of the cationic i.e. quaternary ammonium substituted peroxyacid precursors as disclosed in US Patent 4,751,015

35 and 4,397,757, in EP-A0284292 and EP-A-331,229. Examples of , peroxyacid bleach precursors of this class are:

2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphonphenyl carbonate chloride (SPCC);

N-octyl, N, $N\text{-dimethyl-}N_{10}\text{-carbophenoxy decyl ammonium}$ chloride (ODC);

5 3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

A further special class of bleach precursors is formed by 10 the cationic nitriles as disclosed in EP-A-303,520 and in European Patent Specification No.'s 458,396 and 464,880.

Any one of these peroxyacid bleach precursors can be used in the present invention, though some may be more preferred than others.

Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate

- 25 (SBOBS); N,N,N'N'-tetraacetyl ethylene diamine (TAED);
 sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium4-methyl-3-benzoloxy benzoate; SPCC; trimethyl ammonium
 toluyloxy-benzene sulphonate; sodium nonanoyloxybenzene
 sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyloxyben-
- 30 zene sulphonate (STHOBS); and the substituted cationic nitriles.

The precursors may be used in an amount of up to 12 %, preferably from 2-10 % by weight, of the composition.

Other ingredients

In addition to the ingredients described above, the detergent composition of the invention can contain any of the ingredients conventionally present in compositions

5 intended for the washing of fabrics. Examples of such components include inorganic and organic detergency builders, other inorganic salts such as sodium sulphate, fluorescers, polymers, lather control agents, enzymes and perfumes.

10

35

Other materials that may be present in the powder of the invention include anti-redeposition agents, bleach stabilisers, and photobleaches.

15 The invention will now be illustrated by the following nonlimiting Examples, in which percentages and parts are by weight, unless indicated otherwise.

In these Examples the following abbreviations are used:

- 20 Blanose 7MI sodium carboxymethyl cellulose having a purity of 98%, ex Aqualon;
 - Gabrosa DT732 sodium carboxymethyl cellulose having a purity of 74.5%, ex AKZO-Nobel;
- Symperonic A7 C₁₃-C₁₅ ethoxylated alcohol containing
 an average of 7 ethylene oxide groups per
 molecule, ex ICI;
 - Dobanol 25-7 C_{12} - C_{15} ethoxylated alcohol containing an average of 7 ethylene oxide groups per molecule, ex Shell;
- 30 Dobanol 25-3 C_{12} - C_{15} ethoxylated alcohol containing an average of 3 ethylene oxide groups per molecule, ex Shell;
 - Marlipal 013/50 iso- C_{13} ethoxylated alcohol containing an average of 5 ethylene oxide groups per molecule, ex Hūls;

Ethoxylate 6.5EO - ethoxylated alcohol containing an

WO 97/20020 PCT/EP96/04886

13

average of 6.5 ethylene oxide groups;

Pyramid P50 - amorphous sodium disilicate powder, ex

Crosfield;

TAED - tetraacetyl ethylenediamine.

5

Example 1, Comparative Example A

Two types of builder granules were obtained by granulating zeolite MAP material (as herein defined) with different types of nonionic surfactant and sodium carboxymethyl cellulose (SCMC), in a Patterson-Kelley blendmaster. For carrying out this granulation process, the SCMC is added as

15 a solution in water.

The composition of the thus-formed zeolite MAP granules is as follows:

	Example No.	1	Α
20		(%wt)	(% w t)
	zeolite MAP	72.7	7 2.7
	Blanose 7 M1	3.6	-
	Gabrosa DT 732	-	3.6
	Dobanol 25-7	14.5	-
25	Synperonic A7	-	14.5
	Water	9.2	9.2

The granules of Example 1 contain a CMC compound having a purity according to the present invention whereas the 30 granules of Example A contain a different SCMC compound having a purity below the lower limit of 80% by weight, as specified in the present patent application.

WO 97/20020 PCT/EP96/04886

14

Example 2, Comparative Example B

The zeolite MAP granules of Examples 1 and A were used to prepare particulate detergent formulations, by spraying a surfactant mixture onto said granules and postdosing the 5 other constituents of the formulations.

The thus-prepared formulations which only differ in respect of the composition of the zeolite MAP granules present therein, have the following composition:

10	Example no.	2	В
		(%wt)	(%wt)
	Zeolite MAP ex granules of Example 1	39.4	
	Zeolite MAP ex granules of Example A	-	39.4
	Blanose 7MI ex granules of Example 1	1.9	-
15	Gabrosa DT732 ex granules of Example A	-	1.9
	Dobanol 25-7 ex granules of Example 1	7.9	-
	Synperonic A7 ex granules of Example A	-	7.9
	Dobanol 25-7, sprayed-on	1.1	-
	Synperonic A7, sprayed-on	-	1.1
20	Dobanol 25-3, sprayed-on	6.0	6.0
	Pyramid P50	3.0	3.0
	Oleic acid .	1.5	1.5
	Na percarbonate	20.5	20.5
	TAED	4.5	4.5
25	anti-foam granule	2.0	2.0
	minors	7.1	7.1
	water and salts ex granules	5.0	5.0

30 A dispensing test was carried out with these compositions, according to the following procedure.

A wascator dispenser bank with automatic powder dosing was used. The water intake temperature was set at a constant temperature of 10°C. The water hardness was 6°GH, and the pressure was adjusted at 1.5 bar.

The automatic feeding unit was adjusted such that it doses 100 gr of the particulate detergent composition in 8 seconds in a wet dispenser. A pre-wetting time of 1 minute was applied; subsequently, 8 litre water was dosed in 1 minute (at a pressure of 1.5 bar) to flush the detergent formulation out of the dispenser. After 7 minutes powder dosing was started again. This was repeated 10 times.

Dispenser residues were assessed by weighing the detergent residues remaining in the dispenser after the test. These residues were collected in the wet state.

The result of each dispensing test being the total amount of residue in the form of wet detergent product collected in the dispenser after the test, was expressed as a percentage of the total amount of dry detergent product dosed during the 10 cycles.

Using this method, the following dispensing residue values were obtained.

20	Example No		2	В
	For the composition	including		
	granules of Example	1	0.0	
	For the composition	including		
	granules of Example	A		12.1

25

It can be derived that the dispensing behaviour of the detergent composition of Example 2 including granules according to the present invention is significantly better than the dispensibility of the detergent composition 30 containing granules of Example A.

Example 3, Comparative Example C

Builder granules according to the invention (Example 3)
35 were prepared using the granulation process according to the invention.

WO 97/20020 PCT/EP96/04886

16

For reasons of comparason, commercially available builder granules ex Degussa (tradename: Wessalith) was used

The composition of these zeolite granules is as follows:

5	Example No.	3	С
		(%wt)	(%wt)
	zeolite MAP	76.0	-
	zeolite 4A	-	76.0
	Blanose 7 M1	3.9	-
10	Gabrosa DT 732	-	2.0
	Marlipal 013/50	11.7	· -
	Ethoxylate 6.5 EO	- :	2.6
	Sodium sulphate	-	2.9
	NaOH	-	0.5
15	Water	8.4	16.0

With builder granules having the above shown composition, the so-called black spot test was carried out as follows.

10 grams of the builder granule was added inside a small

20 black cotton wash-rag.

A Siemens Siwamat Plus 3803 washing machine was operated with water having a hardness of 9.4°GH. The wash load being 1 kg of fabric, consisted of 2 kitchen towels, 1 wash towel, 2 pillow cases, and underwear. The black cotton wash 25 rag containing the 10 grams of builder granules was placed on a wash towel inside the machine. The wash load was washed using the wool-wash programme.

After 24 hours, the black cotton wash rag was opened and a visual jugdement was given using, as reference, a photo

30 range: 0= no powder (no white spots visible);

=<2.0: target for domestic powders;</pre>

>3 : unacceptable occurrence of spots.

Furthermore, an "insolubles" test was carried out with the builder granules of Examples 3 and C, using the following method.

10 grams of the builder granule was dissolved in 500 ml
5 water (0°GH, 20°C) by stirring with a magnetic stirrer in a
1 litre beaker glass for 2 minutes, while maintaining a 4
cm vortex. Subsequently, the thus-prepared solution was
filtered through a 125 micron sieve. Thereafter, the sieve
was dried in an oven at 180°C for 15 minutes, and, finally,
10 the sieve was cooled in a desiccator for 20 minutes and
weighed. The amount of insolubles was calculated as a
percentage of the initial amount of builder granules used,
by applying the following equation:

15		(sieve+dried insolubles)-sieve
	% insolubles =	* 100
		amount of granules used

After carrying out the above-described "black spot" and 20 "insolubles" tests using the builder granules of Examples 3 and C, the following results were obtained.

	Example no.			3	С
	"Black spot"	test	result	0.46	2.13
25	"Insolubles"	test	result	5.0	50.5

These results show that the dispersibility of the builder granules of Example 3 is significantly better than of the granules of Example C.

CLAIMS

1. Builder granule suitable for use in a particulate detergent composition, comprising:

5 50-90% by weight of a zeolite;

- 0 -25% by weight of a nonionic surfactant;
- 1 -10% by weight of alkalimetal carboxycellulose having a purity of more than 80% by weight; and up to 20% by weight of water.

10

- 2. Builder granule according to claim 1, wherein the purity of the carboxymethyl cellulose is at least 85% by weight.
- 3. Builder granule according to claim 1 or 2, comprising 3-15 5% by weight of sodium carboxymethyl cellulose.
 - 4. Builder granule according to any of claims 1-3, wherein the nonionic surfactant is a low meso-phase forming type of surfactant (as herein defined).

20

5. Builder granule according to any of claims 1-4, wherein the type of zeolite is maximum aluminium P zeolite (zeolite MAP) having a silicon to aluminium ratio not exceeding 1.33.

- 6. Builder granule according to any of claims 1-5, wherein said granule additionally comprises 0.5-25% by weight of spray-dried amorphous alkalimetal silicate.
- 30 7. Builder granule according to claim 6, wherein said amorphous alkalimetal silicate is sodium silicate having a SiO_2 to Na_2O mol ratio being in the range of 1.7 3.4.
- 8. Builder granule according to any of claims 1-7, wherein 35 the average particle size of said builder granule is in the range of 200-800 micron.

D,

9. Particulate detergent composition, comprising one or more nonionic and/or anionic surfactants and builder granules according to any of claims 1-5.

Interne | I Application No. PCT/EP 96/04886

Îi C 6	C11D3/12 C11D3/22		
	to International Patent (Taspication (IPC) or to both national	classification and IPC	
	OS SEARCHED		
	documentation searched (classification system followed by class	afication symbols)	
Document	ation searched other than minimum documentation to the extent	that such documents are included in the fields	searched
Electronic	data base consulted during the international search (name of da	ta base and, where practical, search terms used)
C. DOCU	MENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of	the relevant passages	Relevant to claim No.
A	EP,A,O 279 038 (DEGUSSA) 24 Au cited in the application see page 3, line 43 - line 51; table 4; claim 1		1-4,8,9
Α	EP,A,O 552 054 (UNILEVER PLC; (NL)) 21 July 1993 see page 2, line 26 - line 29;		5
Α	EP.A.O 260 971 (UNILEVER PLC; (NL)) 23 March 1988 see page 4, line 36 - line 47;		6,7
	1,6,7		
		Patent family members are liste	d in annex
Fu	irther documents are listed in the continuation of box C.	Patent family members are listed	
'A' docu cons 'E' earlie	categories of cited documents: ument defining the general state of the art which is not sidered to be of particular relevance or document but published on or after the international g date	"T" later document published after the user priority date and not in conflict cited to understand the principle or invention. "X" document of particular relevance; the cannot be considered novel or cannot be considered.	with the application but theory underlying the claimed invention
'L' docur whic citati 'O' docur other	ment which may throw doubts on priority claim(s) or this crited to establish the publication date of another ion or other special reason (as specified) ument referring to an oral disclosure, use, exhibition or ir means	involve an inventive step when the 'Y' document of particular relevance; the cannot be considered to involve an document is combined with one or ments, such combination being obvin the art.	document is taken alone ne claimed invention inventive step when the more other such docu-
P docu	ment published prior to the international filing date but than the priority date claimed	"&" document member of the same pate	
	10 February 1997	Date of mailing of the international 1 4, 02, 97	search report
	d mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk	Authonzed officer	
	Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Ainscow, J	

information on patent family members

Intern al Application No PCT/EP 96/04886

				30,04000
Patent document cited in search report	Publication date		t family iber(s)	Publication date
EP-A-0279038	24-08-88	DE-A-	3735618	11-08-88
		AT-T-	106443	15-06-94
		DE-D-	3789971	07-07-94
		DK-A-	19995	24-02-95
		DK-B-	170031	01-05-95
		EP-A-	0368364	16-05-90
		ES-T-	2053935	01-08-94
		JP-B-	6060319	10-08-94
		JP-A-	63193996	11-08-88
	•	US-A-	4883607	28-11-89
EP-A-0552054	21-07-93	AU-B-	647681	24-03-94
		AU-A-	2854692	17-06-93
		AU-B-	662 585	07-09-95
		AU-A-	3181193	29-07-93
		AU-B-	662586	07-09-95
		AU-A-	3181293	29-07-93
		BR-A-	9204572	01-06-93
		BR-A-	9300204	20-07-93
		BR-A-	9300205	20-07-93
		CA-A-	2083331	27-05-93
		CA-A-	2087307	18-07-93
		CA-A-	2087308	18-07-93
		CN-A-	1073713	30-06-93
		CN-A-	1074705	28-07-93
		CN-A-	1074706	28-07-93
		CZ-A-	9204071	19-01-94
		CZ-A-	9204072	19-01-94
		DE-D-	69300710	07-12-95 11-04-96
		DE-T-	69300710	11-04-96
		DE-D- DE-T-	69300873 69300873	18-04-96
		EP-A-	0544492	02-06-93
			0552053	21-07-93
		EP-A- ES-T-	2081173	16-02-96
		ES-1-	2080586	01-02-96
		HK-A-	29596	23-02-96
		HK-A-	29696	23-02-96
	•	HK-A- JP-A-	6080988	22-03-94

Information on patent family members

PCT/EP 96/04886

Patent document cited in search report	Publication date	Patent memb		Publication date
EP-A-0552054	<u></u>	JP-A-	6080989	22-03-94
EP-A-0552054		JP-A-	6100899	12-04-94
		JP-B-	7039599	01-05-95
		KR-B-	9601018	17-01-96
		KR-B-	9601019	17 - 01-96
		NZ-A-	245202	22-12-94
		SK-A-	349592	10-08-94
		SK-A-	407192	10-08-94
		SK-A-	407292	10-08-94
		US-A-	5259981	09-11-93
		US-A-	5259982	09-11-93
		ZA-A-	9300268	15-07-94
		ZA-A-	9300270	15-07-94
EP-A-0260971	23-03-88	AU-B-	583196	20-04-89
EP-A-02009/1	23 03 00	AU-A-	7843787	21-04-88
		CA-A-	1296234	25-02-92
		DE-A-	3778262	21-05-92
		JP-B-	7068554	26-07-95
		JP-A-	63099297	30-04-88
	•	KR-B-	9502354	16-03-95
		TR-A-	25687	01-09-93
	•	US-A-	4965015	23-10-90